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Synthesis, Characterization, and Antibacterial Evaluation of Disubstituted Diphenyldithiophosphate Complexes of Lead (II)

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ABSTRACT

Lead (II) derivatives of disubstituted diphenyldithiophosphates have been synthesized by reaction between lead dichloride and the sodium salt of disubstituted diphenyldithiophosphates in 1:2 molar ratio in chloroform. Adducts with unidentate and bidentate phosphorus and nitrogen-donor molecules, corresponding to the general formula [{(ArO)$_2$PS$_2$}$_2$Pb] and [{(ArO)$_2$PS$_2$}$_2$Pb.nL] (Ar = 4-Cl-3-CH$_3$C$_6$H$_3$, (3,5-CH$_3$)$_2$C$_6$H$_3$); n=2 for P(C$_6$H$_5$)$_3$, NC$_5$H$_5$, n=1 for N$_2$C$_{10}$H$_8$, N$_2$C$_{12}$H$_8$), have been prepared by the straightforward reaction of these complexes with donor ligands. These complexes have been characterized using various physicochemical techniques such as elemental analysis, IR, heteronuclear nuclear magnetic resonance (^{1}H, ^{13}C, and ^{31}P), and mass spectroscopic studies. Coordination numbers of four and six are suggested around the lead atom in these complexes, leading to distorted tetrahedral and octahedral geometries. The antimicrobial activity depicts that these compounds are active against bacteria Gram-positive: Enterococcus faecalis and Bacillus cereus and Gram-negative: Escherichia coli and Klebsiella pneumoniae.

Key words: *Lead, Dithiophosphate, Sulfur, Phosphorus, Antibacterial.*

1. INTRODUCTION

The element lead has been a serious threat to human health as well as a major toxicant for animal and plant species due to its large abundance on earth and multiple uses by humans. Among the three valence states of lead (0, II, and IV), valence state of II is the one most relevant for biology. Lead poisoning is also known as plumbism. Lead additives were patented in 1920s to boost the octane rating of gasoline, and thus increasing fuel efficiency and the performance of engines [1]. The use of antiknocking agent and tetraethyl lead has been discontinued due to the poisonous effect of its combustion products. Lead compounds are also used in paints, cosmetics, and polymer industry [2,3]. The target organs of lead toxicity include the nervous system, kidneys, cardiovascular system, immune system, and reproductive system. Industrial development has resulted in overexploitation of natural resources, and heavy-metal pollution has become one of the most serious environmental problems today. Efforts are being done to reduce the concentration of lead ions in effluent wastewater. These efforts include chemical precipitation, electrodialysis, reverse osmosis, adsorption on organic and inorganic materials, ultrafiltration, solvent extraction and ion exchange [4].

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Sodium salt of diethyldithiophosphate has been a significant lead scavenging agent in wastewater treatment under the brand name of DTP, 7 [5]. Furthermore, the lead toxicity can be treated by chelation therapy using $CaNa_2EDTA$ and dimercaprol as chelating agents [6]. One of the major molecular mechanisms seems to be replacement of zinc with lead in zinc proteins with functional consequences. Calcium-binding proteins are also possible targets. According to Irving-Williams series, lead is the preferred metal in sulfur coordination environments. This feature is important for understanding the affinity of lead for sulfur donor-rich binding sites of zinc in proteins. Since decades, lead has been the metal of interest in several literature reports pertaining to the sulfur-donor ligand complexes [7-11]. Keeping in view the vast literature on lead-sulfur compounds and their role in protecting the environment, we synthesized new disubstituted diphenyldithiophosphate complexes of lead (II).

2. EXPERIMENTAL

2.1. Materials

All the experimental manipulations were carried out under moisture-free conditions using standard Schlenk techniques. Commercial grade chemicals were used for synthetic purposes. Solvents were dried

and distilled before use. The ligands, sodium salts of O,O'-di(4-chloro-3-methyl and 3,5-dimethylphenyl) dithiophosphates, were prepared according to our report [12]. Lead was estimated gravimetrically as PbO_2, and chlorinige was estimated by Volhard's method [13]. Elemental analyses (C, H, N, and S) were measured with the elemental analyzer vario EL-III, their results were found to be in good agreement (±0.3%) with the calculated values. Infrared spectra were recorded in the range of 4000-200 cm^{-1} using pressed KBr pellets on a PerkinElmer spectrum RX1-Fourier transform infrared spectrophotometer. Nuclear magnetic resonance (NMR) samples were prepared in deuteriochloroform ($CDCl_3$). The ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 300 (300 MHz) and reported relative to an internal reference of TMS. The ^{31}P NMR spectra were recorded using H_3PO_4 (85%) as external reference on a Bruker DRX 300 (300 MHz). The ESI mass spectra were recorded on ESQUIRE3000_00037 spectrophotometer.

2.2.1. Synthesis of [{(4-Cl-3-$CH_3C_6H_3O)_2PS_2$}$_2$Pb] (1)

A chloroform solution (~10 mL) of $PbCl_2$ (0.35 g, 1.25 mmol) was added dropwise to a chloroform solution (~30 mL) of [{(4-Cl-3-$CH_3C_6H_3O)_2PS_2$}Na] (1.00 g, 2.49 mmol) with constant stirring at room temperature. The reaction mixture was stirred for 1 h followed by refluxing for 1 h. The turbidity appeared due to the by-product (sodium chloride) was removed by filtration using alkoxy funnel fitted with the G-4 disc, under reduced pressure. Excess of solvent from the filtrate was evaporated *in vacuo* which resulted the complex [{(4-Cl-3-$CH_3C_6H_3O)_2PS_2$}$_2$Pb] (1) as white crystalline in 87% yield. The complex 2 was prepared by the same procedure. The synthetic and analytical details are listed in Table 1.

2.2.2. Synthesis of [{(4-Cl-3-$CH_3C_6H_3O)_2PS_2$}$_2$Pb.2P(C_6H_5)$_3$] (3)

A chloroform solution (~10 mL) of $PbCl_2$ (0.35 g, 1.25 mmol) was added dropwise to a chloroform solution (~30 mL) of [{(4-Cl-3-$CH_3C_6H_3O)_2PS_2$}Na] (1.00 g, 2.49 mmol) with constant stirring at room temperature. The reaction mixture was stirred for 1 h followed by refluxing for 1 h. The turbidity that appeared due to the by-product (sodium chloride) was removed by filtration using alkoxy funnel fitted with G-4 disc, under reduced pressure. A 10 mL methanolic solution of triphenylphosphine (0.64 g, 2.44 mmol) was added dropwise to the above chloroform solution of [{(4-Cl-3-$CH_3C_6H_3O)_2PS_2$}$_2$Pb] (1) with constant stirring. The reaction mixture was refluxed for 1 h. Excess of solvent from the filtrate was evaporated *in vacuo* which resulted in the addition complex [{(4-Cl-3-$CH_3C_6H_3O)_2PS_2$}$_2$Pb.2P(C_6H_5)$_3$], (3) in 89% yield. Addition complexes [{(ArO)$_2PS_2$}$_2$Pb.nL] (Ar = 4-Cl-3-$CH_3C_6H_3$, (3,5-CH_3)$_2C_6H_3$) n=2 for $P(C_6H_5)_3$, NC_5H_5, n=1 for $N_2C_{10}H_8$, $N_2C_{12}H_8$) were prepared by the same procedure. The synthetic and analytical details are listed in Table 1.

2.2. Antibacterial

The antibacterial screening was carried out by agar well diffusion technique [14]. Test samples were prepared in different concentrations (100, 200, 400, and 800 ppm) in dimethyl sulfoxide (DMSO). Agar medium (20 mL) was poured into each petri plate and left to solidify. The plates were then swabbed with broth cultures of the respective four bacterial strains Gram-positive: *Enterococcus faecalis* and *Bacillus cereus* and Gram-negative: *Escherichia coli* and *Klebsiella pneumoniae* and kept for 15 min for adsorption to take place. Using a punch, ≈ 6 mm diameter, wells were bored in the seeded agar plates, and 100 µl of the DMSO solution of each test compound was added into the wells. DMSO was used as the control for all the test compounds as it exhibited no effect on the organism tested, and ciprofloxacin was used as the standard drug. After holding the plates at room temperature for 2 h to allow diffusion of the compounds into the agar, the plates were incubated at 37°C for 24 h. The antibacterial activity was determined by measuring the diameter of the inhibition zone. The entire tests were made in triplicates, and the mean of the diameter of zone of inhibition was calculated.

3. RESULTS AND DISCUSSION

Lead dichloride was reacted with sodium salts of O,O'-di(4-chloro-3-methyl and 3,5-dimethylphenyl) dithiophosphoric acids in dry chloroform in molar ratios of 1: 2, yielding the diaryldithiophosphate complexes of lead(II) formulated as [{(ArO)$_2PS_2$}$_2$Pb] (Scheme 1).

The reaction of the lead dichloride, sodium salts of O,O'-di(4-chloro-3-methyl and 3,5-dimethylphenyl) dithiophosphoric acids, and unidentate donor ligands in 1: 2: 2 molar ratio and with bidentate donor ligands in 1: 2: 1 molar ratio in chloroform yielded the addition complexes corresponding to [{(ArO)$_2PS_2$}$_2$Pb.nL] (Ar = 4-Cl-3-$CH_3C_6H_3$, (3,5-CH_3)$_2C_6H_3$); n = 2 for $P(C_6H_5)_3$, NC_5H_5, n = 1 for $N_2C_{10}H_8$, $N_2C_{12}H_8$) (Scheme 2).

These complexes and adducts are soluble in common organic solvents (toluene, acetonitrile, methanol, and chloroform), however, insoluble in solvents such as n-hexane and carbon tetrachloride. These complexes appear to be bit moisture sensitive; however, these can be kept unchanged under anhydrous atmosphere. These complexes are non-volatile even under the reduced pressure. The elemental analyses (C, H, N, S, Cl, and Pb) were found consistent with the molecular formula of these complexes. These complexes were further characterized by various spectroscopic studies, namely, IR, heteronuclear NMR (^1H, ^{13}C, and ^{31}P),

Table 1: Synthetic and analytical data of diaryldithiophosphates of lead (II) (1-10).

S. No.	Reactants g (mmol)*			Molar ratio	Reflux time (h)	Product (physical state)	Yield (%)	Analysis (%) found (Calcd)					
	L	$PbCl_2$	Donor					C	H	N	S	Cl	Pb
1.	1.00	0.35	-	2:1	1	$[\{(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2\}_2Pb]$	87	34.87	2.48	-	13.28	14.69	21.48
	(2.49)	(1.25)				(white solid)		(34.90)	(2.51)		(13.31)	(14.72)	(21.50)
2.	1.00	0.35	-	2:11	1	$[\{(3,5\text{-}(CH_3)_2C_6H_3O)_2PS_2\}_2Pb]$	85	43.54	4.09	-	14.51	-	23.47
	(2.49)	(1.25)				(white solid)		(43.57)	(4.11)		(14.54)		(23.49)
3.	1.00	0.35	0.64	2:1:2	1	$[\{(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2\}_2Pb.\ 2(P(C_6H_5)_3]$	89	51.62	3.64	-	8.59	9.51	13.89
	(2.49)	(1.25)	(2.44)			(white solid)		(51.65)	(3.66)		(8.62)	(9.53)	(13.92)
4.	1.00	0.35	0.73	2:1:2	1	$[\{(3,5\text{-}(CH_3)_2C_6H_3O)_2PS_2\}_2Pb.\ 2(P(C_6H_5)_3]$	90	58.03	4.71	-	9.10	-	14.71
	(2.49)	(1.25)	(2.78)			(white solid)		(58.06)	(4.73)		(9.12)		(14.73)
5.	1.00	0.35	0.20	2:1:2	1	$[\{(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2\}_2Pb.\ _2NC_5H_5]$	90	40.66	3.01	2.47	11.41	12.61	18.45
	(2.49)	(1.25)	(2.53)			(pale yellow solid)		(40.68)	(3.05)	(2.50)	(11.43)	(12.64)	(18.47)
6.	1.00	0.35	0.22	2:1:2	1	$[\{(3,5\text{-}(CH_3)_2C_6H_3O)_2PS_2\}_2Pb.\ 2NC_5H_5]$	88	48.46	4.44	2.66	12.31	-	19.90
	(2.49)	(1.25)	(2.78)			(pale yellow solid)		(48.49)	(4.46)	(2.69)	(12.33)		(19.92)
7.	1.00	0.35	0.20	2:1:1	1	$[\{(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2\}_2Pb.N_2C_{10}H_8]$	89	40.73	2.84	2.47	11.42	12.63	18.47
	(2.49)	(1.25)	(1.28)			(pale yellow solid)		(40.75)	(2.88)	(2.50)	(11.45)	(12.66)	(18.50)
8.	1.00	0.35	0.22	2:1:1	1	$[\{(3,5\text{-}(CH_3)_2C_6H_3O)_2PS_2\}_2Pb.N_2C_{10}H_8]$	90	48.57	4.25	2.67	12.33	-	19.94
	(2.49)	(1.25)	(1.41)			(pale pink solid)		(48.59)	(4.27)	(2.70)	(12.35)		(19.96)
9.	1.00	0.35	0.22	2:1:1	1	$[\{(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2\}_2Pb.N_2C_{12}H_8]$	90	41.98	2.80	2.42	11.18	12.37	18.08
	(2.49)	(1.25)	(1.22)			(white solid)		(42.00)	(2.82)	(2.45)	(11.21)	(12.40)	(18.11)
10.	1.00	0.35	0.25	2:1:1	1	$[\{(3,5\text{-}(CH_3)_2C_6H_3O)_2PS_2\}_2Pb.N_2C_{12}H_8]$	88	49.73	4.16	2.61	12.05	-	19.48
	(2.49)	(1.25)	(1.39)			(pale pink solid)		(49.75)	(4.18)	(2.64)	(12.07)		(19.51)

L = $(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2Na$ (1,3,5,7,9); $(3,5\text{-}(CH_3)_2C_6H_3O)_2PS_2Na$ (2,4,6,8,10)

Donor=$P(C_6H_5)_3$ (3-4), NC_5H_5 (5-6), $N_2C_{10}H_8$ (7-8) and N2C12H8 (9-10)

and mass. The elemental analyses values are given in Table 1.

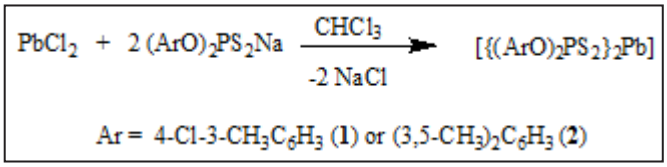
3.1. Spectroscopic Results

3.1.1. Infrared spectroscopic results

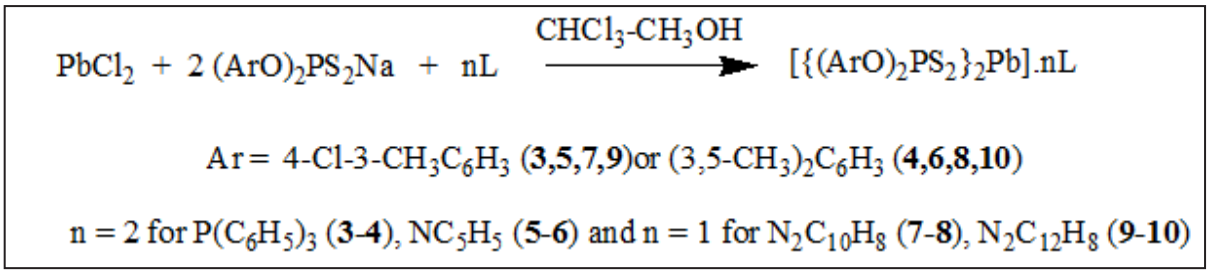
The IR spectra were obtained for the complexes 1-10 to obtain more information about the complex structure. Characteristic IR peaks were assigned in comparison with the previously reported values [7,10,12]. On comparison with the free ligands slight shifting of bands in the IR spectra may be regarded as an evidence of the formation of these complexes The diagnostic vibrational frequencies are two strong intensity bands, ν(P)−O−C, 1178.1-1127.4 cm^{-1}; νP−O−(C), 979.1-954.8 cm^{-1} and two medium intensity bands, νP=S, 872.3-855.5 cm^{-1}; νP−S, 547.6-532.2 cm^{-1}. From the above data, we observe that the $\nu(PS_2)$ signifies anisobidentate binding mode. Furthermore, the presence of a band for νPb−S in the region 391.2-381.3 cm^{-1} in the spectra of these complexes is indicative of the formation of lead-sulfur bond. The addition complexes also indicated weak bands corresponding to stretching vibrations of Pb−P and Pb−N bonds. The νPb−P in triphenylphosphine adducts was found to be in the range of 424.6-419.3 cm^{-1}. While νPb−N was found to lie in the range of 453.1-447.2 cm^{-1} in pyridine adducts, 441.2-436.9 cm^{-1} in bipyridine adducts, and 432.3-427.5 cm^{-1} in 1,10-phenanthroline adducts. The relevant IR spectral data of these complexes are given in Table 2.

3.1.2. NMR spectroscopic results

The ^{1}H NMR spectra ($CDCl_3$) of these complexes have been investigated. Negligible shifting of the characteristic proton resonances of the corresponding aryl protons is observed in complexes in comparison to the ligand protons. The chemical shift for the methyl (−CH_3) protons of the aryl ring was observed in the region 2.1-2.2 ppm as singlet. The chemical shifts for the aryl ring protons were observed in the region 6.5-7.3 ppm as multiplet. Two resonances were observed for the 3,5-dimethylphenyl derivative, whereas the 4-chloro-3-methylphenyldithiophosphato derivatives exhibited three resonances. The addition complexes also



Scheme 1: Synthesis of disubstituted diphenyldithi ophosphate complexes of lead (II).



Scheme 2: Synthesis of addition complexes of disubstituted diphenyldithiophosphate complexes of lead (II) with phosphorus and nitrogen donor ligands.

Table 2: IR spectral data of the diaryldithiophosphates of lead (II) (in cm^{-1}).

S. No.	ν (P)−O−C	νP−O−(C)	νP=S	νP−S	νPb−S	νPb−X
1.	1129.0, s	969.2, s	860.7, s	532.2, m	384.9, w	-
2.	1135.0, s	979.1, s	861.1, s	539.5, m	382.0, w	-
3.	1154.0, s	959.7, s	862.4, s	547.6, m	381.3, w	424.6, w
4.	1163.6, s	956.0, s	858.0, s	544.8, m	384.5, w	419.3, w
5.	1175.0, s	969.3, s	872.3, s	540.6, m	384.9, w	447.2, w
6.	1167.4, s	972.7, s	861.2, s	540.3, m	382.9, w	453.1, w
7.	1178.1, s	959.1, s	869.6, s	545.1, m	384.5, w	441.2, w
8.	1142.7, s	967.4, s	871.5, s	537.8, m	391.2, w	436.9, w
9.	1127.4, s	961.0, s	855.5, s	540.8, m	389.9, w	427.5, w
10.	1157.3, s	954.8, s	866.4, s	540.7, m	387.3, w	432.3, w

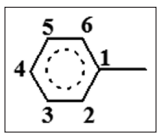
S: Strong, M: Medium, W: Weak, X=P (3-4), X=N (5-10). *The serial number is according to Table 1

exhibited additional peaks for the aromatic protons of the donor ligands. The relevant ^{1}H NMR spectral data of these complexes are given in Table 3.

In these complexes, the phosphorus atom of the dithiophosphate moiety appears as a singlet in the region 91.3-94.5 ppm in the ^{31}P NMR spectra indicating its equivalent nature. This value for ^{31}P nucleus present in these complexes is consistent with anisobidentate behavior of dithiophosphate moiety [7,10,15]. The relevant ^{31}P NMR spectral data of these complexes are given in Table 3.

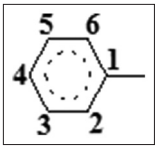
No appreciable change was observed in the ^{13}C NMR spectra of the complexes and has about the same chemical shifts compared to corresponding carbons in the uncoordinated ligand. The chemical shift for the methyl (–CH_3) carbon, attached to aryl ring, was

Table 3: ^{1}H and ^{31}P NMR spectral data of the ditolyldithiophosphates of lead (II) (in ppm).

S. No.	^{1}H NMR			^{31}P NMR
	−CH_3		Donor moiety	
1.	2.19, s, 12 H, CH_3	6.56, s, 4 $H_{(2)}$; 6.46, d, 4 $H_{(5)}$ (J=8.1 Hz); 6.98, d, 4 $H_{(6)}$ (J=8.2 Hz)	-	93.2, s
2.	2.09, s, 24 H, CH_3	6.62, s, 8 $H_{(2,6)}$; 7.21, s, 4 $H_{(4)}$	-	94.5., s
3.	2.17, s, 12 H, CH_3	6.57, s, 4 $H_{(2)}$; 6.48, d, 4 $H_{(5)}$ (J=8.1 Hz); 6.97, d, 4 $H_{(6)}$ (J=8.2 Hz)	7.42-7.71, m, 30 H, P $(C_6H_5)_3$	92.3, s; -5.3*, s
4.	2.18, s, 24 H, CH_3	6.62, s, 8 $H_{(2,6)}$; 7.28, s, 4 $H_{(4)}$	7.31-7.62, m, 30 H, P $(C_6H_5)_3$	91.3, s; -5.4*, s
5.	2.09, s, 12 H, CH_3	6.58, s, 4 $H_{(2)}$; 6.47, d, 4 $H_{(5)}$ (J=8.1 Hz); 6.98, d, 4 $H_{(6)}$ (J=8.2 Hz)	7.29-8.49, m, 10 H, (NC_5H_5)	93.5, s
6.	2.12, s, 24 H, CH_3	6.62, s, 8 $H_{(2,6)}$; 7.26, s, 4 $H_{(4)}$	7.41-8.34, m, 10 H (NC_5H_5)	91.6, s
7.	2.16, s, 12 H, CH_3	6.55, s, 4 $H_{(2)}$; 6.48, d, 4 $H_{(5)}$ (J=8.1 Hz); 6.96, d, 4 $H_{(6)}$ (J=8.2 Hz)	8.12-8.43, m, 8 H $(C_{10}H_8N_2)$	93.7, s
8.	2.19, s, 24 H, CH_3	6.62, s, 8 $H_{(2,6)}$; 7.24, s, 4 $H_{(4)}$	8.22-8.43, m, 8 H $(C_{10}H_8N_2)$	92.6, s
9.	2.12, s, 12 H, CH_3	6.56, s, 6 $H_{(2)}$; 6.47, d, 6 $H_{(5)}$ (J=8.1 Hz); 6.96, d, 6 $H_{(6)}$ (J=8.2 Hz)	7.91-9.02, m, 8 H $(C_{12}H_8N_2)$	94.3, s
10.	2.16, s, 24 H, CH_3	6.62, s, 8 $H_{(2,6)}$; 7.28, s, 4 $H_{(4)}$	8.13-8.91, m, 8 H $(C_{12}H_8N_2)$	93.9, s

s = singlet, d = doublet, t = triplet, m = multiplet, * = chemical shift for P(C6H5)3. *The serial number is according to Table 1.

Table 4: ^{13}C NMR spectral data of the ditolyldithiophosphates of lead (II) (in ppm).

								Donor moiety
								
S. No.	CH_3	C (1)	C (2)	C (3)	C (4)	C (5)	C (6)	
1.	19.0	155.0	113.2	123.3*	135.7’	128.5	116.8	-
2.	21.2	151.6	117.3	138.9*	126.5	138.9*	117.3	-
3.	17.4	155.5	112.3	124.3*	135.4’	128.4	117.4	127.2, 131.2, 132.8, P $(C_6H_5)_3$
4.	22.3	150.4	118.4	137.9*	127.2	137.9*	118.4	127.9, 132.5, 134.2, P $(C_6H_5)_3$
5.	18.2	155.4	113.8	123.7*	134.9’	128.3	116.1	122.6, 139.7, 147.0, NC_5H_5
6.	21.8	150.9	119.5	139.1*	127.1	139.1*	119.5	123.6, 129.3, 146.3, NC_5H_5
7.	19.4	155.1	113.7	126.3*	134.8’	128.4	116.3	121.7, 124.1, 138.2, 148.3, 150.3, $C_{10}H_8N_2$
8.	21.9	150.4	118.9	138.7*	126.4	138.7*	118.9	121.6, 125.1, 138.6, 148.7, 150.1, $C_{10}H_8N_2$
9.	18.9	155.0	113.9	124.3*	135.1’	128.1	116.4	124.0, 124.7, 126.1, 139.1, 150.6, $C_{12}H_8N_2$
10.	21.9	151.4	119.3	138.6*	126.7	138.6*	119.3	122.7, 122.7, 124.1, 137.1, 148.1, $C_{12}H_8N_2$

*C−CH_3, =C−Cl. **The serial number is according to Table 1

found in the region 17.4-22.3 ppm. The carbon nuclei of the aryl ring have displayed their resonance in the region 112.3-155.5 ppm. The aryl carbon nuclei of the triphenylphosphine, pyridine, 2,2′-bipyridine, and 1,10-phenanthroline moiety resonated in the region 128.2-135.2, 123.6-148.0, 120.6-151.3, and 123.7-151.3 ppm. The aryl carbon nuclei of the triphenylphosphine, pyridine, 2,2′-bipyridine, and 1,10-phenanthroline moiety resonated in the region 127.2-134.2, 122.6-147.0, 121.6-150.3, and 122.7-150.6 ppm. The relevant ^{13}C NMR spectral data of these complexes are given in Table 4.

3.1.3. Mass spectroscopic results

The mass spectra of a few representative complexes (1, 4, 5, 8, and 9) have exhibited the presence of molecular ion peak. In addition to the molecular ion peak, several other peaks were also observed, which are corresponding to the fragmented species after the consecutive removal of different groups. The occurrence of molecular ion peak in the complexes is supporting the monomeric nature of the complexes. Furthermore, the complexes (1, 5 and 9) that contain chlorine atom also show isotopic peaks.

The complexes (1, 5, and 9) that contain chlorine atom also show isotopic peaks. Based on the presence of the peaks in the mass spectra of some of the representative complexes, the various fragments have been given in Table 5.

3.2. Antibacterial

The antibacterial screening of these complexes also exhibited significant inhibition of bacterial strains Gram-positive: *E. faecalis* and *B. cereus* and Gram-negative: *E. coli* and *K. pneumoniae* with increasing concentration of the complexes. The observed zone of inhibition for each concentration of the complexes has been given in Table 6, which also shows high antibacterial activity of these complexes against the bacterial strain, especially for *E. coli.* The observed enhancement in antibacterial activity of the metal complexes in comparison to simple ligands can be explained on the basis of Overtone's concept

Table 5: Mass spectral data of the ditolyldithiophosphates of lead (II).

S. No.	MW	m/z, relative intensities of the ions and assignment
1.	963.7	$[M^+]$ 979.0 (10), 981.0 (2) $[\{(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2\}_2Pb]^+$, $[M^+]$ 424.4 (31) $[\{(CH_3C_6H_3O)P(O)S_2\}Pb]^+$, $[M^+]$ 201.3 (56) $[(CH_3C_6H_3O)PS_2]^-$, $[M^+]$ 106.1 (91) $[CH_3C_6H_3O]^-$
2.	1406.3	$[M^+]$ 1406.3 (7) $[\{(3,5\text{-}(CH_3)_2C_6H_3O)_2PS_2\}_2Pb.\ 2P\ (C_6H_5)_3]$, $[M^+]$ 953.9 (34) $[(OPS_2)Pb.\ 2P(C_6H_5)_3]^+$, $[M^+]$ 121.2 (91) $[3,5\text{-}(CH_3)_2C_6H_3O]^-$
3.	1119.9	$[M^+]$ 1119.9 (8), 1121.9 (3) $[\{(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2\}_2Pb.\ 2C_5H_5N]$, $[M^+]$ 821.9 (27) $[\{(CH_3C_6H_3O)_2PS_2\}_2Pb]^+$, $[M^+]$ 308.3 (57) $[(CH_3C_6H_3O)_2PS_2]^+$, $[M^+]$ 278.3 (63) $[(C_6H_3O)_2PS_2]^-$
4.	1038.1	$[M^+]$ 1038.1 (7) $[\{(3,5\text{-}(CH_3)_2C_6H_3O)_2PS_2\}_2Pb.C_{10}H_8N_2]$, $[M^+]$ 474.5 (34) $[(OPS_2)Pb.C_{10}H_8N_2]^+$, $[M^+]$ 121.2 (91) $[3,5\text{-}(CH_3)_2C_6H_3O]^-$
5.	1141.9	$[M^+]$ 1141.9 (8), 1143.9 (3) $[\{(4\text{-Cl-3-}CH_3C_6H_3O)_2PS_2\}_2Pb.C_{12}H_8N_2]$, $[M^+]$ 498.5 (34) $[(OPS_2)Pb.C_{10}H_8N_2]^+$, $[M^+]$ 308.3 (57) $[(CH_3C_6H_3O)_2PS_2]^{+,}$ $[M^+]$ 278.3 (63) $[(C_6H_3O)_2PS_2]^-$

Where, bracket = m/z, parentheses = intensities in %. *The serial number is according to Table 1

Table 6: Antibacterial screening results of the ligands and lead complexes of O, O'-di (4-Cl-3-methylphenyl) dithiophosphates and O, O'-di (3,5-dimethylphenyl) dithiophosphate and their addition complexes with phosphorus and nitrogen-donor bases.

S. No.	Zone of inhibition (cm)															
	Bacteria under investigation															
	Enterococcus faecalis (+)				*Bacillus cereus* (+)				*Escherichia coli* (-)				*Klebsiella pneumoniae* (-)			
1.	100	200	400	800	100	200	400	800	100	200	400	800	100	200	400	800
2.	0.0	0.0	0.0	0.4	0.0	0.0	0.1	0.2	0.0	0.8	1.1	1.4	0.0	0.8	1.3	1.8
3.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.8	1.2	0.0	0.4	1.0	1.1
4.	0.0	0.0	0.4	0.9	0.0	0.5	0.8	1.0	0.4	1.0	1.5	1.6	0.3	1.2	1.6	2.0
5.	0.0	0.0	0.3	0.7	0.0	0.4	0.7	0.9	0.3	1.2	1.6	2.0	0.4	1.1	1.4	1.6
6.	0.0	0.4	0.6	0.8	0.4	0.4	0.7	1.0	0.3	0.8	1.2	1.6	0.4	0.8	1.4	1.5
7.	0.0	0.0	0.4	0.6	0.4	0.4	0.4	0.8	0.1	0.7	1.0	1.4	0.0	0.6	1.2	1.3
8.	0.0	0.1	0.4	0.8	0.0	0.5	0.8	1.0	0.2	1.0	1.4	1.6	0.4	1.1	1.5	1.7

*The serial number is according to Table 1

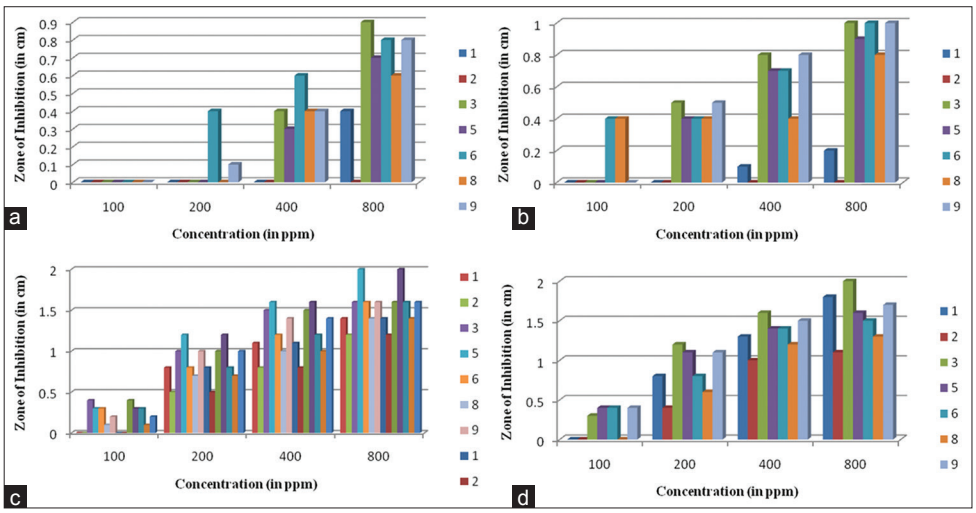


Figure 1: (a) Graphical comparison of antibacterial screening results of all ligands and complexes against Gram-positive bacteria *Enterococcus faecalis*, (b) Graphical comparison of antibacterial screening results of all ligands and complexes against Gram-positive bacteria *Bacillus cereus*, (c) Graphical comparison of antibacterial screening results of all ligands and complexes against Gram-negative bacteria *Escherichia coli*, (d) Graphical comparison of antibacterial screening results of all ligands and complexes against Gram-negative bacteria *Klebsiella pneumoniae*.

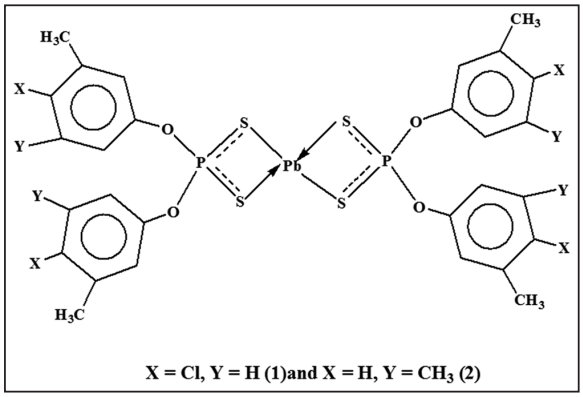


Figure 2: Proposed tetrahedral geometry of the complexes of diaryldithiophosphate compexes of lead(II).

and Tweedy's chelation theory [16]. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only the lipid-soluble materials makes which liposolubility is an important factor, which controls the antibacterial activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of n-electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms. These complexes also disturb the

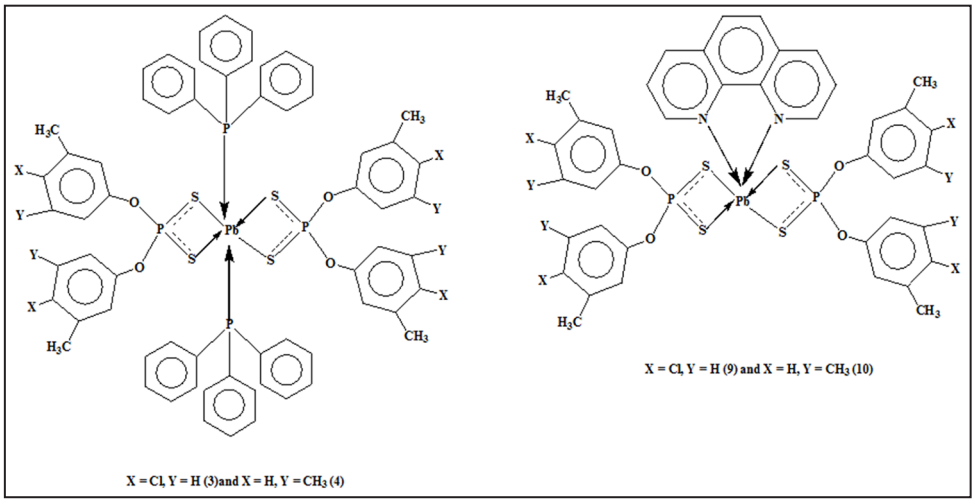


Figure 3: (a) Proposed octahedral geometry of the addition complexes of diaryldithiophosphate compexes of lead (II) with unidentate donor molecule, triphenylphosphine. (b) Proposed octahedral geometry of the addition complexes of diaryldithiophosphate compexes of lead(II) with bidentate donor molecule, 1,10-phenanthroline

respiration process of the cell and thus block the synthesis of the proteins that restricts further growth of the organism. The antibacterial screening data have been tabulated in Table 6, and comparison of antibacterial activity of lead (II) complexes and free ligands is described diagrammatically in Figure 1a-d.

4. CONCLUSION

In conjunction with the literature reports [7-12,15] and observations based on elemental analysis, IR, NMR (^{1}H, ^{13}C, and ^{31}P), and mass spectral studies a probable structure can be assigned to these complexes. The $\Delta\nu$ in the ν(P)−O−C, νP−O−(C), νP=S, and νP−S bands for dithiophosphate moiety in comparison to the parent dithiophosphate ligands indicates the formation of these complexes (1-10). It is interesting to note that appearance of new bands was observed in the IR spectra of these complexes in comparison to the parent dithiophosphate ligands. A new band ascribed to νPb−S is indicative of formation of lead-sulfur bond in these complexes, whereas the formation of adducts was confirmed by the appearance of νPb−P and νPb−N bands. An upfield singlet for the phosphorus atom of the dithiophosphato moiety indicates the anisobidentate mode of chelation by dithiophosphate ligand in addition to the equivalent nature of the phosphorus atom in these complexes. Therefore, distorted tetrahedral and distorted octahedral may be proposed around the lead(II) atom in the complexes (1-2) and the addition complexes (3-10) (Figures 2 and 3a-b), respectively.

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***Bibliographical Sketch**

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